Not all Oxygen is Equal: Identifying the Role of Different Oxygen Functional Groups in the Graphene-Mediated Glutathione Oxidation Reaction

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Glutathione (GSH) is a critical cellular antioxidant that aids in maintaining a healthy redox balance, protecting against the oxidative stress, and minimizing occurrence of disease. As an indicator of oxidative stress, the oxidation of GSH is a facile approach to evaluate (nano)materials and their relative potential to induce adverse biological impacts. Graphene oxide (GO) is a graphene derivative and has attracted significant attention in recent years for wideranging applications. The 2D graphitic structure is decorated with various oxygen functional groups, which can facilitate biophysicochemical interactions at the nano-bio interface. Elucidating these interface interactions provide insight into potential adverse impacts as well as enable many applications in the bioanalytics. Our research aims to further resolve this important biological mechanism by revealing the relative reactivity of the different GO O-groups (—C-O-C, —COOH, —C=O, and —C-OH) towards GSH. Since the GSH reaction on carbon surfaces is dominated by the O_2-mediated catalytic mechanism, we conduct the reaction in the a low O_2 system to isolate the interaction between GSH and specific O-groups. This proposed heterogenous oxidation mechanism changes the GO surface chemistry such that active sites are determined through examination of surface chemistry changes before and after exposure to GSH using XPS. Theoretical support for our empirical findings is provided based on density functional theory calculations of the reaction barriers for all possible GO-GSH reaction schemes, identifying the preferred GSH-O-group reaction(s). The identification of these specific interactions offers additional insight into controlling GO chemical reactivity through surface chemistry manipulations.